KANSAS METHOD FOR THE DETERMINATION OF MID-RANGE HYDROCARBONS (MRH) AND HIGH-RANGE HYDROCARBONS (HRH)

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TABLE OF CONTENTS

Editorial Note: This method is in large part a modification of the Massachusetts Department of Environmental Protection's "Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)." We want to thank that agency for graciously allowing their work to be utilized by others. Since the EPH method has enjoyed a significant amount of direct use by several states, it was determined that it would be best to use it as the base document to establish a method to meet the requirements of the Kansas Department of Health and Environment's Bureau of Environmental Remediation Policy for petroleum cleanup (Policy # BER-041). As needed/warranted, it is expected that this method may be periodically updated as it becomes utilized in Kansas.

METHOD FOR THE DETERMINATION OF MID-RANGE HYDROCARBONS (MRH) AND HIGH-RANGE HYDROCARBONS (HRH)

KANSAS DEPARTMENT OF HEALTH AND ENVIRONMENT

1.0 SCOPE & APPLICATION

1.1 This method is designed to measure the total concentration of extractable petroleum hydrocarbons in water and soil/ sediment matrices. Extractable hydrocarbons are collectively quantitated within two ranges: C_9 through C_{18} (MRH) and C_{19} through C_{35} (HRH). These hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 265 °C.

1.2 This method is designed for a determination of Total Petroleum Hydrocarbon (TPH) in two ranges, MRH and HRH, and/or to obtain qualitative "fingerprinting" information. While TPH provides little information on the chemical constituents, it may be a cost-effective tool.

1.3 This method is based on a solvent extraction and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.4 This method is intended to generate data that may be compared to reporting and cleanup standards promulgated in the Kansas Department of Health and Environment (KDHE) Bureau of Environmental Remediation (BER) Policy # BER-041.

1.5 This method may allow for site-specific cleanup using silica gel. If a site believes they have high aromatic interference, they may request approval from KDHE BER to perform silica gel cleanup and reporting of only aliphatic results. This will be considered on a site-specific basis and must be approved before silica gel cleanup is performed.

1.6 Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuel, and certain lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products which contain a significant percentage of hydrocarbons lighter than C_9. This method, in and of itself, is also not suitable for the evaluation of petroleum products which contain a significant percentage of hydrocarbons heavier than C_{35}.

1.7 The Reporting Limit (RL) of this method for each of the total hydrocarbon ranges is approximately 20 mg/kg in soil/sediment, and approximately 100 µg/L in water.

1.8 This method is one way to quantify total concentrations of extractable petroleum hydrocarbons within specified carbon-number-ranges. It has been designed in a manner that attempts to strike a reasonable balance between analytical method performance and utility. In this manner, assumptions and biases have been incorporated into the method to help ensure protective, though not overly conservative data.

As an example, the KDHE recognizes that branched alkanes have lower boiling points than their n-alkane counterpart, while many of the cycloalkane constituents of diesel range volatile organics have higher boiling points than their n-alkane counterpart. As a consequence:

(1) Depending upon the specific chromatographic column used, most branched C_9 alkanes are expected to elute before n-nonane, the beginning marker compound for the C_9 through C_{18} aliphatic hydrocarbon range, and will not be counted in this range;

(2) Depending upon the specific chromatographic column used, most branched C_{19} alkanes are expected to elute before n-nonadecane, the beginning marker compound for the C_{19} through C_{35} aliphatic hydrocarbon range, and will be conservatively counted in the more toxic C_9 through C_{18} aliphatic hydrocarbon range; and

(3) Depending upon the specific chromatographic column used, most cycloalkanes within the C_9 through C_{18} and C_{19} through C_{35} aliphatic hydrocarbon ranges will be counted within their proper range.

Based on the nature of petroleum releases encountered in the environment, the collective concentrations of the extractable hydrocarbon ranges as measured by the MRH/HRH Method are considered to be suitable for the evaluation of the risks posed by these releases, consistent with the approach developed by KDHE.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for MRH and/or HRH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish apparatus. Optional sample cleanup using commercially available silica gel cartridges or prepared silica gel columns should only be performed with prior approval from KDHE BER. The concentrated extracts are analyzed by a capillary column gas chromatograph equipped with a flame ionization detector. The resultant chromatogram of is collectively integrated within the C_9 through C_{18} and C_{19} through C_{35} ranges.

2.2 Average calibration factors or response factors determined using a hydrocarbon standard mixture are used to calculate the total concentrations of C_9 through C_{18} and C_{19} through C_{35} hydrocarbons.

2.3 This method is suitable for the analysis of waters, soils, sediments, wastes, sludges, and non-aqueous phase liquids (NAPL). However, it should be noted that the source methods were validated only for soil and water matrices.

2.4 This method is based on (1) USEPA Methods 8000B, 8100, 3510C, 3520C, 3540C, 3541, 3545A, 3546, 3580 A and 3630C, SW-846, "Test Methods for Evaluating Solid Waste"; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992, and (4) "Method for the Determination of Extractable Petroleum Hydrocarbons (VPH)," Massachusetts Department of Environmental Protection, Rev 1.1, May 2004.

3.0 DEFINITIONS

3.1 **Analytical Batch** is defined as a group of field samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less is defined as a separate analytical batch.

3.2 **C_9 through C_{18} Mid-Range Hydrocarbons (MRH)** are defined as all hydrocarbon compounds which contain between 9 and 18 carbon atoms and are associated with the release of a petroleum product to the environment. In the MRH method, C_9 through C_{18} hydrocarbons are defined and quantitated as compounds which elute from n-nonane (C_9) to just before n-nonadecane (C_{19}).

3.3 **C_{19} through C_{35} High-Range Hydrocarbons (HRH)** are defined as all hydrocarbon compounds which contain between 19 and 35 carbon atoms and are associated with the release of a petroleum product to the environment. In the HRH method, C_{19} through C_{35} hydrocarbons are defined and quantitated as compounds, which elute from n-nonadecane (C_{19}) to just after n-pentatriacontane (C_{35}).

3.4 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.5 **Continuing Calibration Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The continuing calibration standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.6 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation and storage, as well as laboratory procedures.

3.7 **High-Range Hydrocarbons (HRH)** are defined as the collective fraction of hydrocarbon compounds eluting from n-nonadecane (C19) to just after n-pentatriacontane (C35).

3.8 **High-Range Hydrocarbon (HRH) Standard** is defined as a 10 component mixture of the 8 compounds, one surrogate and one internal standard listed in Table 1. The compounds comprising the HRH Standard are used to (a) define and establish the window for the HRH range, and (b) determine average calibration or response factors that can in turn be used to calculate the collective concentration of hydrocarbons in environmental samples within the C_{19} through C_{35} hydrocarbon range.

3.9 **Mid-Range Hydrocarbons (MRH)** are defined as the collective fraction of hydrocarbon compounds eluting from n-nonane (C9) to just before n-nonadecane (C19).

Table 1. HRH Standard

Carbon Number	Compound	Retention Time (min.)[1]
19	n-Nonadecane	17.95
20	n-Eicosane	19.14
1-Chloro-octadecane	Surrogate	20.13
5-alpha-androstane	Internal Standard	21.25 (estimated)
22	n-Docosane	21.35
24	n-Tetracosane	23.40
26	n-Hexacosane	25.29
28	n-Octacosane	27.04
30	n-Triacontane	28.69
35	n-Pentatriacontane	34.82

[1] Results obtained using the column and chromatographic conditions described in Sections 6.4 and 9.5, respectively.

Table 2. MRH Standard

Carbon Number	Compound	Retention Time (min.)[1]
9	n-Nonane	3.14
10	n-Decane	4.55
12	n-Dodecane	7.86
14	n-Tetradecane	11.10
16	n-Hexadecane	14.05
18	n-Octadecane	16.71
19	n-Nonadecane	17.95

[1] Results obtained using the column and chromatographic conditions described in Sections 6.4 and 9.5, respectively.

3.10 **Mid-Range Hydrocarbon (MRH) Standard** is defined as a 7 component mixture of the compounds listed in Table 2. The compounds comprising the MRH Standard are used to (a) define and establish the window for the MRH range, and (b) determine average calibration or response factors that can in turn be used to calculate the collective concentration of hydrocarbons in environmental samples within the C_9 through C_{18} hydrocarbon range.

3.11 **Initial Calibration Verification (ICV) Standard** is defined as a mid-range standard prepared from a separate source than used for the initial and continuing calibration standards. The analysis of an ICV must be performed when a separate source standard is not used for the preparation of the laboratory control sample and matrix spike sample.

3.12 **Internal Standard** (IS) is a compound added to every calibration standard, blank, matrix spike, sample (for VOAs), sample extract (for semi-volatiles) at a known concentration, prior to analysis. ISs are used as the basis for quantitation of the method's target analytes.

3.13 **Laboratory Control Sample (LCS)** is defined as a reagent water blank (when associated with aqueous samples) or clean sand blank (when associated with soil/sediment samples) fortified with a matrix spiking solution. The LCS is prepared and analyzed in the same manner as the samples and its purpose is to determine the bias of the analytical method.

3.14 **Laboratory Control Sample Duplicate (LCSD)** is defined as a reagent water blank (when associated with aqueous samples) or clean sand blank (when associated with soil/sediment samples) fortified with a matrix spiking solution separately prepared, processed and analyzed in the same manner as the LCS. The analysis of LCS duplicates gives a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.15 **Laboratory Method Blank** is defined as an aliquot of reagent water (when associated with aqueous samples) or clean sand (when associated with soil/sediment samples) spiked with a surrogate standard. The laboratory method blank is prepared and analyzed in the same manner as a sample, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is prepared and analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.16 **Matrix Duplicates** are defined as split samples prepared and analyzed separately with identical procedures. For soil/ sediment samples, matrix duplicate samples are taken from the same sampling container. For aqueous samples, a separate container is used for the matrix duplicate sample. The analysis of matrix duplicates gives a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.17 **Matrix Spike (MS) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The purpose of the MS sample is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of an unspiked sample aliquot. The measured values in the MS sample must be corrected for background concentrations when calculating recoveries of spiked analytes.

3.18 **Matrix Spiking Solution** is defined as a solution prepared from a separate source than used for the calibration standards, containing known concentrations of method analytes.

3.19 **System Solvent Blank** is defined as an aliquot of a method solvent (e.g., hexane or methylene chloride, pesticide-grade or better) that is directly injected into the GC system. The System Solvent Blank provides one way of determining the level of noise and baseline rise attributable solely to the analytical system, in the absence of any other analytes or non-analytical related contaminants.

3.20 **Surrogate Standards** are compounds spiked into all samples, blanks, LCSs, and matrix spikes to monitor the efficacy of sample extraction, chromatographic, and calibration systems.

3.21 All other terms are as defined in the most current version of SW-846, "Test Method for Evaluating Solid Waste", USEPA, or TNI standard.

4.0 INTERFERENCES

4.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Cross-contamination can occur whenever a low-concentration sample is analyzed immediately after a high-concentration sample. To reduce carryover, the sample syringe must be rinsed between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a system solvent blank to check for cross-contamination. However, due to the potential for samples to be analyzed using an autosampler, the ability to perform this blank analysis may not always be possible. If the sample analyzed immediately after the unusually concentrated sample is free from contamination, then the assumption can be made that carryover or cross-contamination is not an issue. However, if this sample did detect analytes which were present in the unusually concentrated sample, reanalysis is required for all samples analyzed after this highly concentrated sample which detected similar analytes.

4.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and complexity of the site being sampled. A silica gel SPE cleanup procedure is used to overcome many of these interferences, but some samples may require additional and more rigorous cleanup procedures which are beyond the scope of this method. Sample cleanup should only be performed with prior approval from KDHE BER on a site/project specific basis.

4.5 Other organic contaminants commingled with petroleum product releases, including chlorinated hydrocarbons, phenols, and phthalate esters, will be quantitated as Total and Extractable Petroleum Hydrocarbons. Additional sample cleanup and/or analytical procedures may be employed to minimize or document the presence of such compounds with prior approval from KDHE BER on a site/project specific basis.

4.6 The leaching of plasticizers and other compounds have been observed from commercially available silica gel cartridges used to fractionate MRH/HRH sample extracts. Concerns of this nature must be continuously monitored and documented by analysis of Laboratory Method Blanks. Section 9.2 provides a procedure to eliminate or minimize this contamination.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following is a partial list of glassware used for this method:

6.1.1 1-L amber glass bottles

6.1.2 4 oz. (120 mL) amber wide-mouth glass jars

6.1.3 Vials:

10.4.4.6 autosampler: 2-mL glass vials with Teflon-lined rubber crimp caps
10.4.4.6 10-mL vials with Teflon-lined caps

6.1.4 Glass funnels

6.1.5 2-L Separatory funnels with Teflon stopcock (aqueous liquid-liquid extraction only)

6.1.6 Kuderna-Danish apparatus including 10-mL graduated concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column

6.1.7 250-mL Erlenmeyer flasks

6.1.8 25-mL graduated cylinder

6.1.9 1-Liter graduated cylinder

6.1.10 100-mL beakers

6.1.11 Class “A” volumetric flasks: 10, 25, 50 and 100-mL

6.1.12 Class “A” volumetric pipets: 1, 5 or 10-mL

6.2 An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil/sediment samples.

6.3 An air or nitrogen blowdown apparatus, or equivalent sample concentration apparatus, is required to concentrate extracts.

6.4 Gas Chromatographic System

6.4.1 Gas Chromatograph: An analytical system incorporating a temperature-programmable oven with the ability to accommodate a capillary column. The following components are also required:

6.4.1.1 Detector: A Flame Ionization Detector (FID) is required.

6.4.1.2 Column: The analytical column must adequately resolve the n-C_9 to n-C_{35} hydrocarbon standard compounds listed in Tables 1 and 2. The recommended analytical column is an RTX-5 capillary column (30-m x 0.32-mm i.d., 0.25-µm film thickness [Restek Corp. or equivalent]).

6.4.1.3 Data Station: The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.4.1.4 Autosampler: An autosampler capable of making 1 to 4 µL injections is recommended.

6.5 Water bath: heated with a concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

6.6 Disposable pipets: Pasteur

6.7 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

6.8 Boiling Chips

6.9 Soxhlet, Soxtec or alternative extraction apparatus

6.10 Drying oven

6.11 Dessicator

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic free water (ASTM Type I reagent grade water).

7.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide-grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.1.5 Silica Gel (5 - 10 grams), either prepared and packed by the laboratory, or purchased in 5 g/20-mL cartridges from a commercial vendor. Silica gel prepared and packed by the laboratory should be activated at 130ºC for at least 16 hours, and heated to 150-160ºC for several hours before use. Refer to Section 9.2.2 for guidance on the use of silica gel. Use only if approved by KDHE BERon a site/project specific basis.

NOTE: Leaching of plasticizers and other compounds have been observed from commercially prepared silica gel cartridges, and must be monitored and documented by analyses of Laboratory Method Blanks. Refer to Section 9.2 for a procedure to eliminate or minimize this contamination.

NOTE: **Silica gel is hygroscopic**. Unused cartridges readily absorb moisture from ambient air if not properly sealed. To preclude moisture adsorption, which adversely effects cartridge performance, unused cartridges must be stored in a properly-maintained dessicator prior to use.

7.2 **Stock Standard Solutions**

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

7.2.1 Hydrocarbon Standards: The Hydrocarbon Standards consist of the compounds listed in Table 1 and Table 2, and a surrogate compound (i.e., 1-chloro-octadecane). Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask.

7.2.2 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.2.3 Calibration standards are prepared by serial dilution of the stock standard as described in Section 9.7.2.1.

7.3 **Petroleum Reference Spiking Solution**

7.3.1 The Petroleum Reference Spiking Solution consists of an API or commercial diesel fuel standard. Prepare stock standard solutions by accurately weighing approximately 0.02500 g of neat product. Dissolve neat product in acetone and dilute to volume in a 10-mL volumetric flask. An appropriately diluted aliquot of the stock solution may be used to evaluate method performance.

7.4 **Surrogate Standards**

7.4.1 Surrogate standards are used to monitor the efficiency of sample extraction, chromatographic, and calibration systems.

7.4.2 The recommended surrogate standard is chloro-octadecane (COD, available from Restek Corporation, Bellefonte, PA). Alternatively, 5-alpha-androstane may also be used as an aliphatic fraction surrogate without qualification.

7.4.3 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane.

7.4.4 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of the COD surrogate standard. Prepare a surrogate spiking solution which contains the surrogate standard at a concentration of 40 ng/µL in acetone or methanol. Each sample, blank, and matrix spike is fortified with 1.0 mL of the surrogate spiking solution. The use of higher concentrations are permissible and advisable when spiking highly contaminated samples.

7.5 **Internal Standards (ISs)**

7.5.1 Internal standards are compounds with similar physical and chemical properties, and chromatographic compatibility with an analytical method's target analytes. ISs are added to all samples, both for analysis and quality control, at a known concentration and carried through the entire analytical process (extraction and analysis). Internal standards are used as the basis for quantification of target analyte compounds and ranges. For the MRH/HRH Method, ISs are only utilized when GC/MS is utilized for quantification.

7.5.2 The recommended IS for the MRH/HRH Method is 5-alpha-androstane (EM Sciences, Gibbstown, NJ) for hydrocarbon range concentrations using GC/MS. Alternatively, 1-Chloro-octadecane (COD) may also be used as an internal standard for GC/MS analysis.

7.5.3 The internal standard is prepared by accurately weighing approximately 0.0500 grams of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride or hexane.

7.5.4 An aliquot of 10 µL of the internal standard stock standard is added to the 1 mL MRH/HRH sample extract prepared in accordance with Section 9.3. Alternative concentrations/volumes of the internal standard spiking solution are permissible.

7.6 **Matrix Spiking Solution**

7.6.1 The spiking solution, consisting of all compounds in Table 1 and Table 2 and prepared using a separate source from the calibration standards, is prepared in methanol or acetone at concentrations between 50 - 150 ng/µL (The concentration should be between the mid and upper level of calibration).

7.6.2 The samples selected as the matrix spike are fortified with 1.0 mL of the matrix spiking solution.

Analytical Note: The Matrix Spiking Solution should always be brought to room temperature before use to avoid dissolution of the highest boiling (marginal solubility) hydrocarbon standards.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 **Aqueous Samples**

8.1.1 It is good practice to instruct field personnel to collect aqueous samples in duplicate. Samples must be collected in 1 liter amber glass bottles with Teflon-lined screw caps.

8.1.2 Aqueous samples must be preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This may be accomplished by the addition of 5 mL of 1:1 HCl to a 1 liter sample. The uses of alternative acids are permissible. Following collection and addition of acid, the sample must be cooled to 4± 2° C.

8.1.3 A chain of custody form must accompany all sample bottles and must document the date and time of sample collection and preservation method used. The laboratory must determine the pH of all water samples as soon as possible after sample receipt and prior to sample extraction. Any sample found to contain a pH above 2 must be so noted on the laboratory/data report sheet and the pH must be adjusted as soon as possible.

8.1.4 Any sample received by the laboratory that is not packed in ice or cooled to 4± 2° C must be so noted on the laboratory report. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.1.5 Aqueous samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

8.2 **Soil/Sediment Samples**

8.2.1 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with Teflon-lined screw caps.

8.2.2 Soil and sediment samples must be cooled to 4 ± 2° C immediately after collection.

8.2.3 A chain of custody form must accompany all sample bottles and must document the date and time of sample sample collection and preservation method used.

8.2.4 Any sample received by the laboratory that is not packed in ice or cooled to 4±2° C must be so noted on the laboratory report. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.2.5 Soil and sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

8.2.6 Alternatively, samples may be frozen (-10°C) in the field or in the laboratory. Samples frozen in the laboratory must be preserved at 4 ± 2° C from the time of sampling and frozen within 48 hours.

8.3 A summary of sample collection, preservation, and holding times is provided in Table 3.

Table 3. Holding Times and Preservatives for MRH/HRH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl; Cool to 4 ± 2° C	Samples must be extracted within 14 days and extracts analyzed within 40 days
Soil/Sediment Samples	4-oz. (120 mL) wide-mouth amber glass jar with Teflon-lined screw cap	Cool to 4 ± 2° C	Samples must be extracted within 14 days and extracts analyzed within 40 days of extraction
	4-oz. (120 mL) wide-mouth amber glass jar with Teflon-lined screw cap. Jar should be filled to only 2/3 capacity to avoid breakage if expansion occurs during freezing	Freeze at - 10°C in the field or in the laboratory*.	Samples must be extracted within 14 days of the date thawed and extracts analyzed within 40 days of extraction.

* Samples processed in the laboratory must be preserved at 4 ± 2° C and frozen within 48 hours of the time of collection. Frozen samples may be held for up to one year prior to analysis and must be extracted within 24 hours of thawing.

9.1 Overview of Sample Extraction Procedures

Samples are extracted using methylene chloride and solvent-exchanged into hexane. MRH/HRH extraction may be accomplished manually or by automated methods. In this Section a detailed description of manual separatory funnel liquid-liquid extraction for aqueous samples (SW-846 Method 3510) and the Soxhlet extraction procedure (SW-846 Method 3540) for soils and/or sediments are presented to demonstrate general extraction concepts for petroleum products. The applicable SW-846 Method should be consulted for specific details for the other approved MRH/HRH extraction procedures

NOTE: For optimum performance, the sample volumes/weights, solvent volumes, and final extract volumes cited in Sections 9.1.1 and 9.1.2 are recommended. Alternate volumes can be used as long as comparable reporting limits are achieved.

The complete list of approved MRH/HRH extraction procedures for water and soil/sediment samples is presented in Table 4. Alternative extraction procedures other than those listed are acceptable, provided that the laboratory can document acceptable matrix- and petroleum product-specific performance. However, use of an alternative extraction procedure is considered a "significant modification" of the MRH/HRH method pursuant to Section 11.3.1.1 and as such would preclude obtaining "presumptive certainty" status for any analytical data produced using an alternative MRH/HRH extraction procedure.

Table 4 - Approved MRH/HRH Extraction Methods

SW-846 Method	Matrix	Description
3510C	Aqueous	Separatory Funnel liquid-Liquid Extraction
3520C	Aqueous	Continuous Liquid-Liquid Extraction
3511	Aqueous	Organic Compounds in Water by Microextraction
3540C	Soil/Sediment	Soxhlet Extraction
3541	Soil/Sediment	Automated Soxhlet Extraction
3545A	Soil/Sediment	Pressurized Fluid Extraction (PFE)
3546	Soil/Sediment	Microwave Extraction
3570	Soil/Sediment	Microscale Solvent Extraction (MSE)
3550C	Contaminated Solids [1]	Ultrasonic Extraction
3580A	NAPL	Solvent Dilution
1. Sonication may only be used for extraction of highly contaminated (free product) non-soil/sediments (debris). Any other use of ultrasonic extraction is considered a **"significant modification"** of the MRH/HRH Method.		

9.1.1 Water Extraction by Separatory Funnel Liquid-Liquid Extraction

9.1.1.1 Mark the meniscus on the 1 liter sample bottle (for later volume determination) and transfer the contents to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. For all samples, blanks, LCSs, LCSDs and matrix spikes add 1.0 mL of the concentrated surrogate spiking solution (see Section 7.4) directly to the separatory funnel. For samples selected for spiking, also add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample must be adjusted to pH <2.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for at least three (3) minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask.

9.1.1.6 Repeat the extraction two more times using additional 60 mL portions of solvent. Combine the three solvent extracts in a 250-mL Erlenmeyer flask. (Steps 9.1.1.3 to 9.1.1.5).

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked and transfer this water to a graduated cylinder.

9.1.1.8 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.1.9 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate or other suitable drying agent. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 to 30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

9.1.1.10 Add one or two clean boiling chips to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.11 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column. Concentrate the extract to less than 10 mL, as described in Section 9.1.1.10, raising the temperature of the water bath, if necessary, to maintain proper distillation.

9.1.1.12 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto an air blowdown apparatus. Adjust the extract volume to 1 mL under a gentle stream of nitrogen or air. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. Unless site/project specific prior approval has been granted to perform silica gel cleanup, proceed to Section 9.3.3.

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C9 through C12) MRH components. The extract volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.1.1.13 For cleanup, refer to Section 9.2.

9.1.2 Soil and/or Sediment Extraction using Soxhlet Extraction

9.1.2.1 Blend 10 g of the solid sample with 10 g anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. Add 1.0 mL of the surrogate spiking solution (see Section 7.4) to all samples, blanks, LCSs, LCSDs and matrix spikes. Thoroughly mix the surrogate spiking solution into the sample. For samples selected for spiking, add 1.0 mL of the matrix spiking solution. Thoroughly mix the matrix spiking solution(s) into the sample.

9.1.2.2 Place 300 mL of methylene chloride into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hr. Volume of methylene chloride should be adjusted to accommodate the size of the round-bottom flask utilized.

9.1.2.3 Allow the extract to cool after the extraction is completed.

9.1.2.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate or other suitable drying agent. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of methylene chloride to complete the quantitative transfer.

9.1.2.6 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column. Concentrate the extract to less than 10 mL, as described in Section 9.1.2.6, raising the temperature of the water bath, if necessary, to maintain proper distillation.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto an air blowdown apparatus. Adjust the extract volume to 1 mL under a gentle stream of nitrogen or air. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. Unless site/ project specific prior approval has been granted to perform silica gel cleanup, proceed to Section 9.3.3.

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C9 through C12) MRH components. The extract volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.1.2.9 For cleanup, refer to Section 9.2.

9.2 **Silica Gel Cleanup**

NOTE: Sample cleanup should only be performed with prior approval from KDHE BER on a site/ project specific basis. The Silica Gel Cleanup step is a critical and highly sensitive procedure. Small changes in the volumes of eluting solvents, equipment, and/or techniques can significantly impact the proportion of hydrocarbons eluted. Considerable care and attention is required to ensure satisfactory results.

9.2.2 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions.

A 5 g/20 mL Solid Phase Extraction (SPE) silica gel cartridge is commercially available. Alternatively, the use of self-packed columns of activated silica gel may also be used. The use of activated silica gel for general column chromatographic applications is described in detail SW-846 Method 3630C

To ensure satisfactory cleanup, silica gel/cartridges must not be overloaded. It is recommended that loading be limited to no more than 5 mg total hydrocarbons/gram silica gel; for a 1 mL extract fractionated on a 5 gram silica gel cartridge, this would equate to a hydrocarbon extract loading of no greater than 25,000 µg/mL.

Unsealed silica gel/cartridges must be stored in a properly-maintained dessicator to avoid inadvertent adsorption of ambient moisture. Silica gel that has been exposed to moisture may perform erratically resulting in poor performance.

Analytical Note: Air-drying the cartridge may adversely affect silica gel performance and is not advised.

9.2.3 If concerns exist over the presence of contaminants in the silica gel/cartridge, pre-rinse the column with 30 mL of methylene chloride.

9.2.3.1 Rinse the column with 30 mL of hexane, or 60 mL if pre-rinsed with methylene chloride per Section 9.2.3. Let the hexane flow through the column until the head of the liquid in the column is just above the column frit. Close the stopcock to stop solvent flow. Discard the collected hexane.

9.2.3.2 Load 1.0 mL of the combined sample extract and fractionation surrogate solution onto the column. Open the stopcock, and start collecting elutant immediately in a 25-mL volumetric flask.

9.2.3.3 Just prior to exposure of the column frit to the air, elute the column with an additional 19 mL of hexane, so that a total of approximately 20 mL of hexane is passed through the column.

It is essential that "plug flow" of the sample extract be achieved through the silica gel cartridge/ column. Hexane should be added in 1-2 mL increments or dropwise using a pipet, with additions occurring when the level of solvent drops to the point just prior to exposing the column frit to air. The use of a stopcock is mandatory. Care must be taken to ensure that the silica gel is uniformly packed in the column. The analyst must be cognizant of any channeling, streaking, or changes in the silica gel matrix during fractionation; if any of these occur, the procedure must be repeated with another 1 mL volume of sample extract.

The amount of hexane used during elution is critical. Insufficient hexane will cause low recoveries. The volume of the hexane elutriate should not exceed 20 mL.

9.3 **Final Sample Extract Concentration**

9.3.1 Transfer the contents of the 25.0 mL volumetric flask into labeled graduated concentrator tube. Concentrate the extract to a final volume of 1 mL under a gentle stream of air or nitrogen.

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C9 through C12) MRH components. The extract volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.3.2 Transfer the final 1 mL extract from the concentrator tube to labeled two-mL glass autosampler vials with Teflon-lined rubber crimp caps. If appropriate, add an internal standard at the appropriate concentration.

9.3.3 Proceed with the analysis. Analyze all laboratory method blanks and QC samples under the same conditions as those used for samples.

9.4 **Determination of Percent Moisture**

9.4.1 Soil and sediment results must be reported on a dry-weight basis.

9.4.2 Transfer 5 to 10 g of sample into a tared (± 0.1 g) crucible and determine "wet weight". This sample must be obtained from a vial or container that does not contain methanol. Dry this 5 to 10 g sample overnight at 105°C. Allow crucible to cool in a dessicator and reweigh (± 0.1 g). Re-desiccate and verify "dry weight". Calculate the percent moisture of the sample using the equations provided in Section 9.9.4 (Equation 9). Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

9.5 **Analytical Conditions**

9.5.1 Recommended analytical conditions are presented below. A chromatographic column with equivalent chromatographic properties, as described in Section 6.4.2, or alternative chromatographic conditions may be substituted to improve resolution of extractable petroleum hydrocarbons.

Chromatographic Column:	30 m x 0.32 mm I.D., 0.25 µm Restek RTX-5
Oven Temperature Program:	Initial oven temperature 60°C, hold time 1 min; to 290 °C @ 8°C/min, hold time 6.75 min
Total Run Time:	36.5 min
Sample/autosampler Injection:	1-4 uL

Gas Flow Rates:	Carrier gas - Helium @ 2 to 3 mL/min Oxidizer - Air @ 400 mL/min Fuel – Hydrogen @ 35 mL/min Make up – Air @ 30.0 mL/min
Injection Port Temperature:	285°C
Column Inlet Pressure:	15 p.s.i.g.
Detector Temperature:	315°C (FID)
Linear Velocity	50 cm/sec

9.5.2 GC Maintenance

9.5.2.1 Capillary columns: Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert.

9.5.2.2 Break off the first few inches, up to one foot, of the injection port side of the column.

9.5.2.3 Remove the column and solvent backflush according to the manufacturer's instructions.

9.5.2.4 Bake out the column at the maximum temperature of the temperature program. If these procedures fail to eliminate a column degradation problem, it may be necessary to replace the column.

9.6 **Retention Time Windows**

9.6.1 Before establishing retention time windows, optimize the GC system's operating conditions. Make three injections of the hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too restrictive.

9.6.2 Calculate the standard deviation of the absolute retention times for each individual component in the standard mixture and all surrogates and internal standards.

9.6.3 The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each compound in the standards. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.6.4 In those cases where the standard deviation for a particular standard is close to zero the default value of 0.1 minutes should be used. Alternatively, the laboratory may substitute the standard deviation of a closely eluting structurally similar compound to develop a representative statistically-derived retention time window.

9.6.5 The laboratory must calculate retention time windows for each compound in the standard on each GC column and whenever a new GC column is installed. These data must be retained by the laboratory.

9.6.6 MRH/HRH retention time (Rt) windows are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound, except for n-C_{19}, which is both a beginning and ending marker compound for two different ranges.

The C_9 - C_{18} Hydrocarbon range ends immediately (0.1 min) before the elution of the n-C_{19} peak. The C_{19} - C_{35} Hydrocarbon range begins 0. 1 min before the elution of the n-C_{19} peak; therefore there is no overlap of the two ranges and the n-C_{19} peak is only included in the C_{19} - C_{35} Hydrocarbon range.

MRH and HRH marker compounds and windows are summarized in Table 5.

Table 5. MRH and HRH Marker Compounds

Hydrocarbon Range	Beginning Marker	Ending Marker
C_9-C_{18} Hydrocarbons	0.1 min before n-Nonane	0.1 min before n-Nonadecane
C_{19}-C_{35} Hydrocarbons	0.1 min before n-Nonadecane	0.1 min after n-Heptatriacontane

9.7 **Calibration**

9.7.1 Internal Standard Calibration Procedure

An internal standard calibration procedure is not recommended for this method except when GC/MS is used to quantify hydrocarbon ranges (see Section 9.10).

9.7.2 External Standard Calibration Procedure

The use of Calibration Factors (CF) is the preferred approach to determine the relationship between the detector response and the analyte and collective range concentrations. It is also permissible to utilize linear regression to calculate the slope and y-intercept that best describes the linear relationship between the analyte and collective range concentrations and the instrument response using appropriate formulas.

9.7.2.1 Prepare Hydrocarbon calibration standards from the Stock Standard Solution (in methanol) at a minimum of five concentrations (i.e., 1x, 10x, 50x, 100x and 200x) by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with hexane. The lowest concentration (1x) determines the minimum working range of the calibration curve. The highest concentration (200x) defines the maximum upper working range of the calibration curve.

RLs for hydrocarbon ranges are discussed in Section 12.0 The total concentrations of individual MRH and HRH ranges are provided in Table 6.

Table 6. Recommended Calibration Standard Concentrations (1 µL Injection)

Component	Conc. of standard analytes (ng/µL)				
	1	10	50	100	200
Total Concentration C_9 - C_{18} Hydrocarbons (7 components)	6	60	300	600	1200
Total Concentration C_{19} - C_{35} Hydrocarbons (8 components)	8	80	400	800	1600

9.7.2.2 Introduce each calibration standard into the gas chromatograph using the injection volume (e.g., 1 to 4 µL) that will be used to introduce the "actual" samples and following the procedures outlined in Section 9.8.

9.7.2.3 Hydrocarbon Range Calibration (External Standard): A calibration factor must be established for each hydrocarbon range of interest. Calculate the CFs for C_9-C_{18} Hydrocarbons and C_{19}-C_{35} Hydrocarbons from the appropriate FID chromatogram. Tabulate the summation of the peak areas of all components in that fraction (i.e. C_9-C_{18} Hydrocarbons, 7 components) against the total concentration injected. The results can be used to calculate the ratio of the peak area response summation to the concentration injected, defined as the CF, for the hydrocarbon ranges using Equation 3. The %RSD of the calibration factor must be equal to or less than 25% over the working range for the hydrocarbon range of interest, as determined using Equation 2.

A listing of the collective nominal concentrations of standards within each hydrocarbon range is provided in Table 6.

Note: For the calculation of calibration factors (CFs):

The area for the surrogates must be subtracted from the area summation of the range in which they elute (e.g., COD is subtracted from the C_{19} - C_{35} Hydrocarbon range).

Equation 3: Range Calibration Factor: Hydrocarbon Ranges

$$Range\ CF = \frac{Area\ Summation\ of Range Components}{Total\ concentration\ injected\ (ng/\mu L)}$$

9.7.2.4 At a minimum, the calibration factor must be verified on each working day, after every 20 samples or every 24 hours (whichever is more frequent), and at the end of the analytical sequence by the injection of a mid-level continuing calibration standard to verify instrument performance. If the percent difference (%D) for any analyte varies from the predicted response by more than ±25%, as determined using Equation 4, a new five-point calibration must be performed for that analyte. Greater percent differences are permissible for n-nonane. If the %D or percent drift for n-nonane is greater than 30, note the nonconformance in the case narrative It should be noted that the %Ds are calculated when CFs are used for the initial calibration and percent drifts are calculated when calibration curves using linear regression are used for the initial calibration (see Section 10.4.3.1).

Equation 4: Percent Difference (%D)

$$\%D = \frac{CF_{AVG} - CF_{CC}}{CF_{AVG}} \times 100$$

where:

CF_{AVG} = Average Calibration Factor calculated from initial calibration.
CF_{CC} = Calibration Factor calculated from continuing calibration standard.

9.7.2.5 For MRH/HRH analysis, calibration factors are developed based upon the response of the components associated with their respective ranges using Equation 3.

9.8 **GC Analysis**

9.8.1 Samples are analyzed in a group referred to as an analytical batch. For methods that require extraction prior to analysis, such as MRH/HRH, the number of samples that comprise an analytical batch is generally limited to 20 samples plus the requisite QC samples processed concurrently with the extraction batch. The analytical sequence begins with instrument calibration (initial or continuing) followed by up to 20 samples interspersed with blanks and other QC samples and closed with a mid-range continuing calibration standard. The analytical sequence ends when one or more analytical batches have been processed or when any required qualitative and/or quantitative QC criteria are exceeded.

9.8.2 Extracts are introduced into the gas chromatograph by direct injection.

9.8.3 Inject 1 to 4 µL of the sample extract using the solvent flush technique. Smaller volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL and the resulting peak size in area units. It is required that the sample and calibration standard injection volume be consistent.

9.8.4 Establish daily retention time windows for each analyte or range of interest. Use the absolute retention time time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.6. Alternatively, the default value of 0.1 minutes may be used for the daily retention time window.

9.8.4.1 Tentative identification of an analyte occurs when a peak from a sample chromatogram falls within the daily retention time window. Confirmation on a second GC column or by GC/MS analysis may be necessary, if warranted by project's data quality objectives.

9.8.4.2 Validation of GC system qualitative performance must be accomplished by the analysis of mid-level standards within the analysis sequence. If the retention times of the analytes fall outside their daily retention time window in the standards, the system is out of control. In such cases, the cause of the non-conformance must be identified and corrected.

9.8.5 Hydrocarbon ranges of interest are determined by the collective integration of all peaks that elute between specified range "marker" compounds. Due to the variability in software approaches and applications to collective peak area integration, it is recommended that a manual verification be initially performed to document accurate integration.

9.8.6 **When quantifying on a peak area basis by external calibration, collective peak area integration for the fractional ranges must be from baseline (i.e. must include the unresolved complex mixture "hump" areas).** For the integration of individual analytes, surrogate compounds, and internal standards, a valley-to-valley approach should typically be used, though this approach may be modified on a case-by-case basis by an experienced analyst. In any case, the unresolved complex mixture "hump" areas must not be included in the integration of individual analytes, surrogate compounds, and internal standards.

9.8.7 Baseline correction using a system solvent blank is **only** permissible for the calculation of hydrocarbon range concentrations when conducted in accordance with the procedures and requirements specified in Section 11.2.5.

9.8.8 If individual analytes are to be quantitated using this method, and the response for an individual analyte exceeds the highest calibration concentration, dilute the extract and reanalyze. Samples must be diluted so that all peaks fall within the calibration range of the detector and are bracketed by upper and lower calibration standards.

9.8.9 For non-target analytes, the upper linear range of the system should be defined by peak height measurement based upon the maximum peak height documented for a standard within the fraction that is shown to be within the linear range of the detector.

9.8.10 Analytical conditions that require sample dilution include;

1. The concentration of one or more individual analytes of interest exceed the concentration of their respective highest calibration standard,
2. Any non-target peak eluting within any range exceeds twice the peak height documented for the highest range-specific calibration standard, or
3. Anytime a saturated chromatographic peak (flat-topped peak) is encountered

When sample extracts are diluted, the Reporting Limit (RL) for each target analyte and/or range must be adjusted (increased) in direct proportion to the Dilution Factor (DF). Where:

$$DF = \frac{\text{Sample Extract Volume (mL)} + \text{Diluent Volume (mL)}}{\text{Sample Extract Volume (mL)}}$$

And the revised RL for the diluted sample, RL_d:

RL_d = DF X Lowest Calibration Standard for individual analyte of interest or hydrocarbon range

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy program reporting limits in some cases if the RL_d is greater than the applicable criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample extract dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the analytical report.

Analytical Note: Over dilution is an unacceptable laboratory practice. The target post-dilution concentration for the highest concentration target analyte should be at least 60 - 80% (must be at least 50%) of its highest calibration standard. This will avoid unnecessarily high reporting limits for other target analytes, which did not require dilution.

9.9 **Calculations**

9.9.1 External Standard Calibration

The concentration of individual analytes and hydrocarbon ranges in a sample may be determined by calculating the concentration of the analyte or hydrocarbon range injected, from the peak area response, using the calibration factor determined in Section 9.7.2. Linear regression may used for calibration, using appropriate formulas.

9.9.2 Aqueous Samples (External standard):

The concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using Equations 5 and 6, respectively.

Equation 5: Aqueous Samples (Individual Analytes: External Standard)

$$Conc\ Analyte\ (\mu g/L) = \frac{(A_x)(D)(V_t)}{(CF)(V_s)}$$

Equation 6: Aqueous Samples (Hydrocarbon Ranges: External Standard)

$$Conc\ HC\ Range\ (\mu g/L) = \frac{(A_x)(D)(V_t)}{(Range\ CF)(V_s)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample. Units must be in area counts for individual analytes and must be an area count summation for the hydrocarbon ranges.

D = Dilution factor*; dimensionless.

CF = Average Calibration Factor for individual analyte, determined in Section 9.7.2.3

Range CF = Average Calibration Factor for hydrocarbon range, determined in Section 9.7.2.4.

V_t = Volume of total extract, µL (fractionation + surrogate volume)

V_s = Volume of sample extracted, mL.

Non-aqueous samples (External Standard):

The concentration of a specific analyte or hydrocarbon range in a non-aqueous sample may be calculated using Equations 7 and 8, respectively.

Equation 7: Non-Aqueous Samples (Analyte of Interest: External Standard)

$$Conc\ Analyte\ (ug/kg) = \frac{(A_x)(V_t)(D)}{(W_d)(CF)}$$

Equation 8: Non-Aqueous Samples (Hydrocarbon Ranges: External Standard)

$$Conc\ HC\ Range\ (ug/kg) = \frac{(A_x)(V_t)(D)}{(W_d)(Range\ CF)}$$

where: W_d = Dry weight of sample, g (see Equations 9 through 11)

A_x, V_t, D, CF, and Range CF have the same definition as described above for Equations 5 and 6.

9.9.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.4. Using the data obtained from Section 9.4, W_d is calculated using Equations 9 through 11.

Equation 9: Percent Moisture

$$\%\ Moisture = \frac{g\ wet\ sample - g\ dry\ sample}{g\ wet\ sample}\ X\ 100$$

Equation 10: Percent Solids

$$\%\ Dry\ Solids\ =\ (100)\ -\ (\%\ Moisture)$$

Equation 11: Dry Weight of Sample

$$W_d\ (g)\ =\ (\%\ Dry\ Solids / 100)(g\ of\ extracted\ sample)$$

9.10 **Determination of Individual Analytes and MRH/HRH Range Concentrations by Gas Chromatography/ Mass Spectrometry (GC/MS)**

Individual analytes and hydrocarbon ranges may be quantified using GC/MS under this method and not considered a "Significant Modification", as described in Section 11.3.1.1, by satisfying the following requirements:

9.10.1 Individual analytes must be identified, quantified and satisfy the QC requirements and performance standards of SW-846 Method 8270C with the modifications listed below. For quantification of the MRH and HRH ranges the MS detector must be operated in the Total Ion Current mode.

9.10.2 Modified SW-846 Method 8270C QC Requirements for MRH and HRH Analysis*

* All referenced Section numbers refer to SW-846 Method 8270C .

9.10.2.1 DFTPP must be used as a tuning standard (Section 5.5).

9.10.2.2 5-alpha-androstane (using m/z 245 as primary quantitation ion) is the recommended internal standard, other internal standards may be used, as appropriate.

9.10.2.3 Evaluation of DDT breakdown, and Pentachlorophenol and Benzidine tailing is not required.

9.10.2.4 Range Calibration Factors must be based on all the individual calibration standards described in Tables 1 and 2, that are included within the specified range as defined by the MRH and HRH marker compounds described in Table 5. Range Calibration Factors are determined by dividing the summation of the peak areas (Total Ion Current) for all individual calibration standard components that elute within a specified range (i.e., C9 – C18 Aliphatic Hydrocarbons, 6 components) by the total concentration injected.

9.10.2.5 Evaluation of the System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC) alone, as described in Sections 7.3.4 and 7.3.5, respectively, are insufficient to verify calibration. All target analytes must be evaluated in the ICAL and CCV and meet the performance standards described in Table 7 below.

9.10.2.6 Evaluation of Continuing Calibration Standard (equivalent to the CCV described in SW-846 Method 8270C) standards is required at the beginning and end of each analytical sequence,

9.10.2.7 The analytical batch for MRH/HRH analyses may include the analysis of up to 20 samples completed within 12 hours of the batch's tune.

9.10.2.8 The performance standards for the MRH and HRH Ranges and comparable performance standards are presented below in Table 7. In addition to these performance standards, the performance standards must also meet the requirements of SW-846 Method 8270C.

Table 7. Modified SW-846 Method 8270C Analytical QC Requirements and Performance Standards for MRH and HRH Range Analyses

QC ELEMENT	PERFORMANCE STANDARD MRH/HRH Range Data
Initial Calibration (% RSD)	≤ 25
Opening CCV (%drift)	≤ 25
Closing CCV (%drift)	≤ 25
Method Blanks	< RL
Internal Standard (IS)	Area Count of IS must be within 50 and 200% of associated Opening Calibration
Surrogate Recovery	40 – 140%
Laboratory Control Sample (LCS)	40 –140%
LCS Duplicate (RPD)[1]	< 25
Matrix Spike (MS)/MS Duplicate	40 –140%; RPD ≤ 50
1. At discretion of data user	

9.10.3 The sample must be extracted using the procedures described in Section 9.1 and the resultant concentrated extract fractionated as described in Section 9.2.

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method is required to operate a formal quality control program in accordance with the most current version of the TNI standard. The minimum requirements of this program consist of an initial demonstration of capability (iDOC) and an ongoing analysis of spiked samples to evaluate and document the quality of data. The initial demonstration of capability should be repeated whenever new staff are trained or significant changes in instrumentation or the method (i.e., new extraction method, etc.) are made. The laboratory must maintain records to document data quality. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the analytical system was in-control when the measurements were performed.

10.1.2 A system solvent blank must be run after all highly contaminated samples to minimize the potential for sample carryover. For purposes of this analytical requirement, any sample with an on-column concentration greater than the highest calibration standard is considered "highly contaminated" (see Section 4.4).

10.1.3 Batch Analytical Quality Control Samples

10.1.3.1 At a minimum, for each analytical batch (up to 20 samples) or every 24 hours, whichever comes first, a beginning and ending Continuing Calibration Standard must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range Continuing Calibration Standard should also be considered. However, it should be noted that the analysis of the Continuing Calibration Standard is required prior to sample analysis, after every 20 samples or every 24 hours, whichever come first, and at the end of an analytical sequence, at a minimum.

10.1.3.2 At a minimum, for each analytical batch (up to 20 samples of similar matrix), a Laboratory Method Blank, a Laboratory Control Sample (LCS), and a LCS Duplicate must also be analyzed and results analyzed as part of the laboratory's continuing quality control program. The blank and quality control samples fortified with known concentrations and volumes of analytical standards should be carried through the complete sample preparation and measurement processes.

10.1.3.3 It should be noted that field QC samples (field blanks, duplicates, matrix spikes and matrix spike duplicates) are run on pre-identified field samples at the request of the data user. Coordination with the laboratory is required to assure that adequate sample volume is available.

10.1.4 The recommended analytical sequence is as follows:

(1) Analytical Batch Opening Initial Calibration or mid-range Continuing Calibration Standard **[REQUIRED]**
(2) Initial Calibration Verification **[REQUIRED*],**
***** only if separate-source standard not used for LCS**]**
(3) Extraction Batch Laboratory Control Sample **[REQUIRED]**
(4) Extraction Batch Laboratory Control Sample Duplicate [As requested by data user]
(5) Extraction Batch Laboratory Method Blank **[REQUIRED]**
(6) Up to 20 Samples
(7) Matrix Duplicate sample [As requested by data user]
(8) Matrix Spike/MS Duplicate **[REQUIRED]**
(9) Optional mid-range Continuing Calibration Standard (consider after 10 samples)
(10) Closing mid-range Continuing Calibration Standard after 20 samples and at end of analytical batch **[REQUIRED]**
a. May be used as Analytical Batch Opening Continuing Calibration for the next analytical batch if batches are processed continuously.

10.1.5 It is recommended that surrogate standard recoveries be monitored and documented on a continuing basis. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 40% or more than 140%, check calculations to locate possible errors, check the fortifying solution for degradation, and check for changes in instrument performance. If the cause cannot be determined, re-extract and re-analyze the sample if the recovery of Reextraction and reanalysis are not required if one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture); and
(2) If the surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limits to evaluate applicable data quality standards can still be achieved with the dilution. If not, reanalysis without dilution must be performed.

10.2 **Minimum Instrument QC**

10.2.1 The instrument must be able to achieve adequate separation and resolution of peaks and analytes of interest.

10.2.1.1 The n-nonane (n-C_9) peak must be adequately resolved from the solvent front of the chromatographic run.

10.2.1.2 The surrogate COD must be adequately resolved from any individual components in the standards.

10.2.1.3 All peaks of interest in the standard must be adequately resolved to baseline.

For the purposes of this method, adequate resolution is assumed to be achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks.

10.2.2 Retention time windows must be re-established for individual analytes each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Sections 9.6 and 9.8.4).

10.2.3 Calibration curves, calibration factors, or response factors must be developed based upon the analysis calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the %RSD over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation (i.e., calibration curve), the correlation coefficient (r) must be at least 0.99. (See Section 9.7).

10.3 **Initial and Ongoing Demonstration of Capability (iDOC)**

An initial demonstration of capability must be conducted, successfully completed and documented prior to reporting any samples by the LRH Method. An iDOC shall be completed each time there is a change in instrument type, personnel, or method. The laboraotry shall also have a documented procedure for ongoing DOC. All DOC procedures shall be performed according to the most current version of the TNI standard.

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, LCS, LCSD, MS, and Matrix Duplicate must be fortified with the surrogate spiking solution. Required surrogate recovery is 40% to 140%. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 40% or more than 140%, check calculations to locate possible errors, check the fortifying solution for degradation, and check for changes in instrument performance. If the cause cannot be determined, reextract and reanalyze the sample if the recovery of one surrogate is <40% or the recoveries of both surrogates are outside the acceptance limits. Re-extraction and reanalysis are not required if one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture); and
(2) If the surrogate exhibits high recovery and associated analytes or hydrocarbon ranges are not detected in sample.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limits to evaluate applicable data quality standards can still be achieved with the dilution. If not, reanalysis without dilution must be performed.

10.4.3 At a minimum, with every batch of 20 samples or less the laboratory must extract and analyze the following quality control samples:

10.4.3.1 **Continuing Calibration Standard** - A mid-range continuing calibration standard, prepared prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range continuing calibration standard is recommended after the analysis of the tenth sample. However, it should be noted that a mid-range continuing calibration standard is required after every 20 samples or every 24 hours (whichever comes first) and at the end of the analytical sequence. If the percent difference or percent drift of any analyte within the continuing calibration standard varies from the predicted response by more than 25%, a new five-point calibration must be performed for that analyte. Greater differences are permissible for n-nonane. If the percent difference or percent drift is greater than 30% for n-nonane, note the nonconformance in the laboratory report. For the closing continuing calibration standard (analyzed after every 20 samples, every 24 hours, or at end of analytical sequence), four compounds may exhibit percent differences or percent drifts greater than 25% but less than 40%.

10.4.3.2 **Initial Calibration Verification** – An Initial Calibration Verification standard, prepared from a separate source standard than used for initial and continuing calibrations, must be analyzed prior to sample analysis if a separate source standard is <u>not</u> used for the LCS. The recoveries of all individual analytes of interest must be between 80-120%. A new five-point calibration must be performed if criteria are not met.

10.4.3.3 **Laboratory Control Sample** - A Laboratory Control Sample is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution. The spike recovery must be between 40% and 140%. Lower recoveries of n-nonane are permissible. If the recovery of n-nonane is <30%, note the nonconformance in the laboraotry report. Reextraction of all associated samples is required if criteria are not met.

10.4.3.4 **Laboratory Method Blank** - A water or soil Laboratory Method Blank is prepared by fortifying a reagent water or clean sand blank (optional) with 1.0 mL of the surrogate spiking solution. Peaks must not be detected above the Reporting Limit within the retention time window of any analyte of interest. The hydrocarbon ranges must not be detected at a concentration greater than 10% of the most stringent cleanup standard. Peaks detected within the retention time window of any analyte or range of interest above a Reporting Limit must be noted on the laboratory report. Re-extraction of all associated samples may be warranted.

10.4.3.5 **Matrix Spike/Matrix Spike Duplicate** - The water or soil MS is prepared by fortifying an actual water or soil sample with 1.0 mL of the matrix spiking solution. The desired spiking level is 50% of the highest calibration standard. However, the total concentration in the MS (including the MS and native concentration in the unspiked sample) should not exceed 75% of the highest calibration standard in order for a proper evaluation to be performed. The purpose of the matrix spike is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate unspiked aliquot and the measured values in the matrix spike corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 40 - 140% of the true value. Lower recoveries of n-nonane are permissible, but must be noted in the laboratory report if <30%.

10.4.3.6 **System Solvent Blank** - If baseline correction will be employed, as specified in Section 11.2.5, a system solvent blank, air blank, and/or system run must be undertaken with every batch, and after the analysis of a sample that is suspected to be highly contaminated. In no case shall baseline correction be used if the instrument baseline drift is more than 25% greater than the average level established by these charts.

10.4.4 At the request of the data user, and in consideration of sample matricies and data quality objectives, matrix spikes and matrix duplicates may be analyzed with every batch of 20 samples or less per matrix.

10.4.4.1 **LCS Duplicate** – A Laboratory Control Sample Duplicate is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution (see Section 7.7 and Tables 1 and 2). The LCS Duplicate is separately prepared, processed and analyzed in the same manner as the LCS and is used as the data quality indicator of precision. The Analytical Batch Precision is determined from the Relative Percent Difference (RPD) of the concentrations (not recoveries) of LCS/LCSD pair. The RPD for individual analytes and hydrocarbon range concentrations (sum of the individual compounds within the specified range) must be ≤ 25.

10.4.4.2 **Matrix duplicate** - Matrix duplicates are prepared by analyzing one sample in duplicate. The purpose of the matrix duplicates is to determine the homogeneity of the sample matrix as well as analytical precision. The RPD of detected results in the matrix duplicate samples must not exceed 50 when the results are greater than 5x the reporting limit.

10.4.5 If any of the performance standards specified in Section 10.4 are not met, the cause of the non-conformance must be identified and corrected before any additional samples may be analyzed. Any samples run between the last QC samples that met the criteria and those that are fallen out must be re-extracted and/or re-analyzed. These QC samples include the opening continuing calibration standard, laboratory method blank, LCS, LCSD, and closing continuing calibration standard. If this is not possible, that data must be reported as suspect.

10.4.6 The analyte and hydrocarbon range Reporting Limits should be verified/re-established at least once per year, or upon a major change in system equipment or operations (see Section 10.1.1).

11.0 DATA PRODUCTION AND REPORTING

11.1 **Calibration**

Using the external standard calibration procedure (9.7.2) calibrate the GC as follows:

11.1.1 Calculate a CF for the surrogate, COD.

11.1.2 Calculate a collective CF or LR for the total concentration of the C_9 -C_{18} MRH Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C_9-C_{18}, 6 components) against the total concentration injected. Do not include any areal contribution of the internal standard.

11.1.3 Calculate a collective CF or LR for the total concentration of the C_{19} -C_{35} HRH Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C_{19}-C_{35} Aliphatics, 8 components) against the total concentration injected. Do not include the surrogate COD.

11.2 **Sample Analysis**

11.2.1 Mid-Range Hydrocarbons (MRH)

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-C_9 and 0.1 minutes before the Rt for n-C_{19}. It is not necessary to identify or quantitate individual compounds within this range.

11.2.1.2 Determine the peak area count for any surrogate and internal standards used. Subtract these values from the collective area count value.

11.2.1.3 Using the equations contained in Section 9.9, calculate the concentration of MRH.

11.2.2 High-Range Hydrocarbons (HRH)

11.2.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time Rt) for (n-C_{19} and 0.1 minutes after the Rt for n-C_{35}. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.2.2 Determine the peak area count for any surrogate and internal standards used. Subtract these values from the collective area count value.

11.2.2.3 Using the equations contained in Section 9.9, calculate the concentration of HRH.

11.2.3 Baseline Correction for Instrument Noise Level

11.2.3.1 MRH and HRH hydrocarbon range area data determined by the collective integration of all eluting peaks between the specified range marker compounds (see Table 5) may be corrected by the manual or automatic subtraction of the baseline established by the injection of a System Solvent Blank. Correction in this manner is not recommended or preferred, but is permissible in cases where all reasonable steps have been taken to eliminate or minimize excessive baseline bias associated with analytical system noise.

11.2.3.2 The instrument baseline must be established by the direct injection of a system solvent blank. The injection of an air blank or activation of a temperature programmed chromatographic run without the injection of any material should be used to verify that the system noise is not attributable to solvent contamination. All system operational elements and parameters must be identical to those of a typical sample run.

If baseline correction is used, the baseline must be re-established for every analytical batch by the analysis of a System Solvent Blank. Baseline correction may not be used for any sample for which the area count associated with the baseline correction is greater than 10% of the uncorrected area count for the sample's corresponding collective range.

12.0 REPORTING LIMITS

The RLs for hydrocarbon ranges shall be based upon the concentration of the lowest calibration standard for an individual analyte within the range of interest. The range RL will be set at 100x the concentration of the lowest calibration standard for the associated analyte. Calculated total concentrations for MRH and HRH ranges below the RL should be reported as < Range RL (i.e., < 100 ug/L).

Based on the on-column concentration of 1 ηg/µL for the lowest calibration standard for all analytes, the following reporting limits would be generated for the hydrocarbon ranges:

Aqueous Samples: MRH and HRH range reporting limits would be equivalent to 100 µg/L based on the extraction of 1 liter of sample, a final fractionation extract volume of 2 mL, and a sample injection volume of 1 µL.

Soil/Sediment Samples: MRH and HRH range reporting limits would be equivalent to 20 mg/kg (dry weight basis) based on the extraction of 10 grams of soil, a final fractionation extract volume of 2 mL, and a sample injection volume of 1 µL.

13.0 REFERENCES

1. MADEP and ABB Environmental Services, Inc., "Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter", August, 1994.

2. MADEP, “Final Updated Petroleum Hydrocarbon Fraction Toxicity Values For the VPH/EPH/APH Methodology”, January 2003.

3. USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual" Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

4. USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 3510C, 3520C, 3540C, 3541, 3545A, 3546, 3580A, 3630C, 8000B, 8100

5. USEPA Federal Register 40 CFR Part 136, Appendix B, "Guidelines Establishing Test Procedures for the Analysis of Pollutants", July 1992.

6. Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics", PUBL-SW-141, 1992

7. USEPA, “Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring”, EPA 821-B-93-001; U.S. Government Printing Office, Washington D.C., June, 1993

8. Massachusetts DEP, “Report on the Results of the Fall 1997 VPH/EPH Round Robin Testing Program”, December, 1997

9. EPA UST Workgroup, Draft "Method for Determination of Diesel Range Organics", November, 1990

10. ASTM 1990. Standard Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock, *Annual Book of ASTM Standards*, D 2216-90 (revision of 2216-63, 2216-80).

APPENDIX 1

CHROMATOGRAMS

Figure 1 Gas Chromatogram (FID) of the Alkane Component Standard (20 μg/L)

Figure 2 Gas Chromatogram (FID) of a Diesel Standard (Aliphatic Fractions)

Note: These are representative chromatograms were taken from one of the source methods. The hydrocarbon ranges in the chromatograms are similar, but differ slightly from the ranges required by this method.

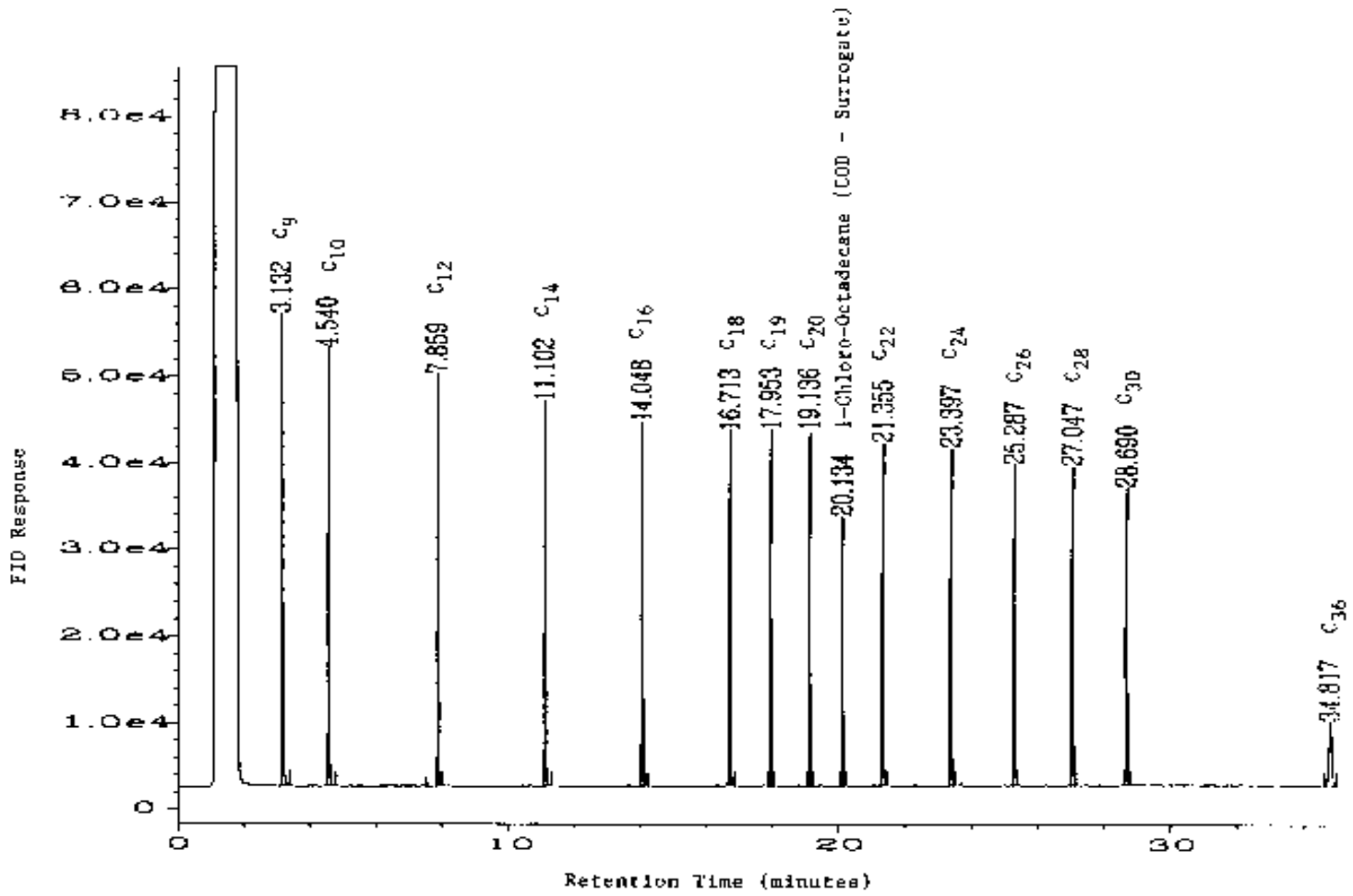

Figure 1. Gas Chromatogram of the Alkane Diesel Component Standard (20 µg/mL).

RTX-5 capillary column (30-m x 0.32-mm i.d., 0.25-µm film thickness); FID at 315°C; splitless injection of 2 µL at 285°C; oven programming, 60°C (hold 1 min) to 290°C at 8°C/min (hold 6.75 min); helium column flow, 2-3 mL/min; helium makeup flow, 30 mL/min; air flow 400 mL/min; hydrogen flow 35 mL/min; electronic pressure control of 15 psi at 60°C.

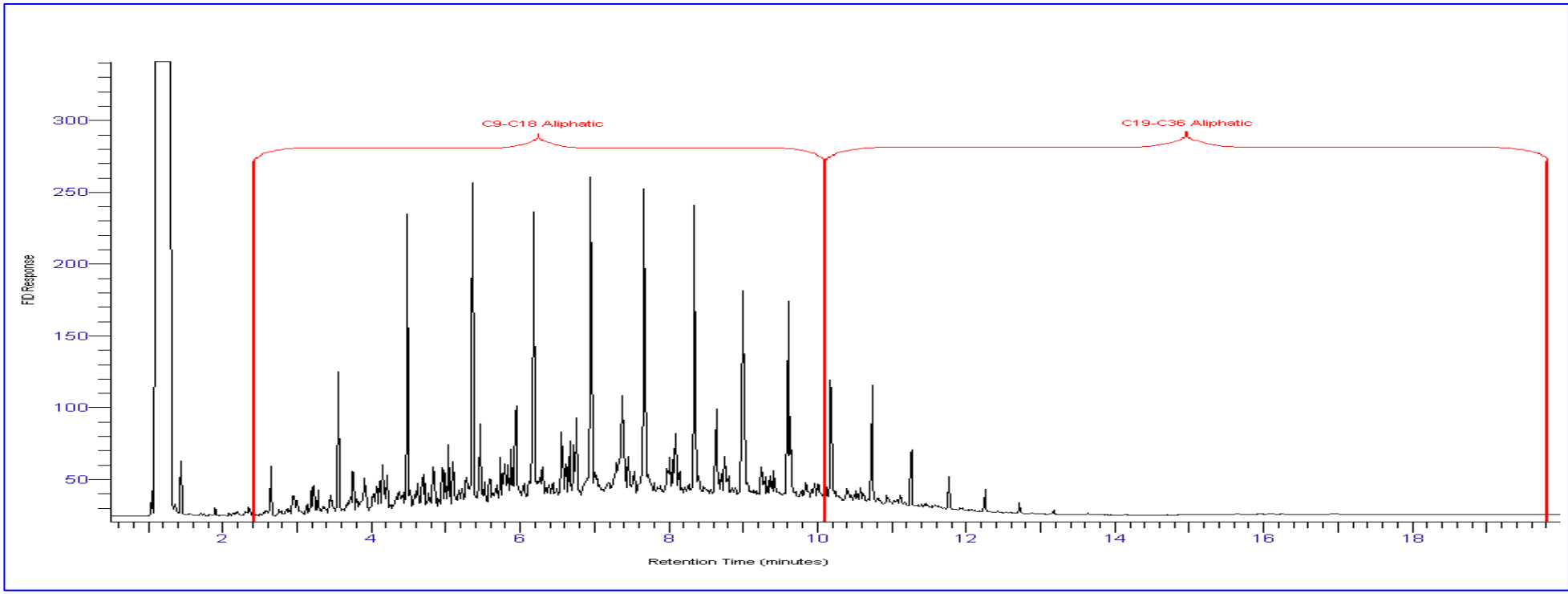

Figure 2 Gas Chromatogram (FID) of a Diesel Standard (Aliphatic Fractions)

Restek RTX-5 SIL-MS capillary column (30 meters .32mm .25 microns); FID detector on a HP 5890 Series II.